

REMARKS

By the present amendment, claims 1, 6, 7 and 11 have been amended to obviate the examiner's objections thereto and/or to further clarify the concepts of the present invention. Entry of these amendments is respectfully requested.

In the Office Action, it was indicated that one of the references cited in the Information Disclosure Statement of July 27, 2004, had not been considered since the PCT Search Report was in Japanese and no concise explanation of the reference was provided.

While it is submitted that this requirement is not necessary since an English language copy of the Search Report apparently was provided with the Information Disclosure Statement, an abstract and machine translation of the reference are submitted herewith. No representations are made as to the accuracy of the machine translation.

Claims 1-11 were rejected under the second paragraph of 35 USC § 112 as being indefinite. Specifically, the following was alleged along with applicants' response thereto:

(1) In claim 1, the phrase "molecular weight," without further modification, was alleged to be unclear. Given that the definition of "MFR" states that the styrene composition has a weight average molecular weight, claim 1 has been amended to be consistent with lines 21-23 of page 17 of the specification.

(2) In claim 1, the phrase "melt flow rate" was alleged to be unclear without a recitation of conditions. Further, the terms "MFR" and "melt tension" were alleged to require units. In response, the formulae of claim 1 have been amended in accordance with the disclosure at pages 18 and 19 of the specification.

(3) In claim 1, it was alleged that the quantity with an exponent in inequality (1) has units and, as such, is mathematically meaningless. In response, it is urged that, while molecular weight technically has units of weight per weight mole, it may generally be considered to be a ratio and not to have units.

(4) In claim 1, the inequality (2) has different units on each side and as such was asserted to be contradictory. It is submitted that the response to item (3) would be applicable to this item as well.

(5) In claim 6, the identity of "n" was not stated. Claim 6 has been amended to be in conformance with line 2 of page eight of the specification.

(6) In claim 7, the phrase "double bonds connected directly to an aromatic ring" was alleged to be impossible since the ring would have five double bonds. It would appear that the same situation applies to claims 4 and 5 as well. Specific examples of compounds having such double bonds are those styrenes set forth in lines 3-6 of page nine of the specification and which have the structure of Aryl-C=C- . Thus, it would appear that which was intended was the portion of noted phrase "double bonds" means the groups of the structure -C=C- which forms the double bond.

(7) In claim 6, the term "aryl" was alleged to be inaccurate and it was suggested that the term "arylene" be substituted therefor. Claim 6 has been amended as suggested.

(8) In claims 7 and 11, the phrase "caring out" was alleged not to be art recognized and was therefore unclear. These claims have been amended to recite the more appropriate phrase "carrying out" instead.

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OA dated 4/20/05
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Accordingly, withdrawal of the rejection under the second paragraph of 35 U.S.C. § 112 is respectfully requested.

In view of the foregoing, it is submitted that the subject application is now in condition for allowance and early notice to that effect is earnestly solicited.

In the event this paper is not timely filed, the undersigned hereby petitions for an appropriate extension of time. The fee for this extension may be charged to Deposit Account No. 01-2340, along with any other additional fees which may be required with respect to this paper.

Respectfully submitted,

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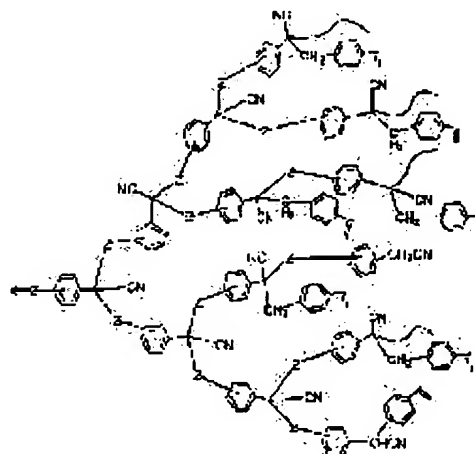
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(54) COPOLYMER OF STYRENE DENDORIMER AND OLEFIN AND METHOD FOR PRODUCING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a novel copolymer of a styrene dendorimer and an olefinic compound which is soluble in a solvent and has a high molecular weight, and to provide a method for producing the copolymer.

SOLUTION: The novel copolymer wherein a styrene dendorimer represented by formula (I) (wherein X is a halogen atom, p-CH₃PhSO₃ group or hydroxyl group; Z is -(OCH₂CH₂)_n, -O(CH₂)_n or -OCH₂Ph (n is an integer of 1 to 12, the terminal oxygen atom is bound to o-, m- and p-position of a benzen ring) and the olefinic compound are subjected to a radical copolymerization to bind the olefinic compound with a double bond of a styrene residue and the method for producing the same.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

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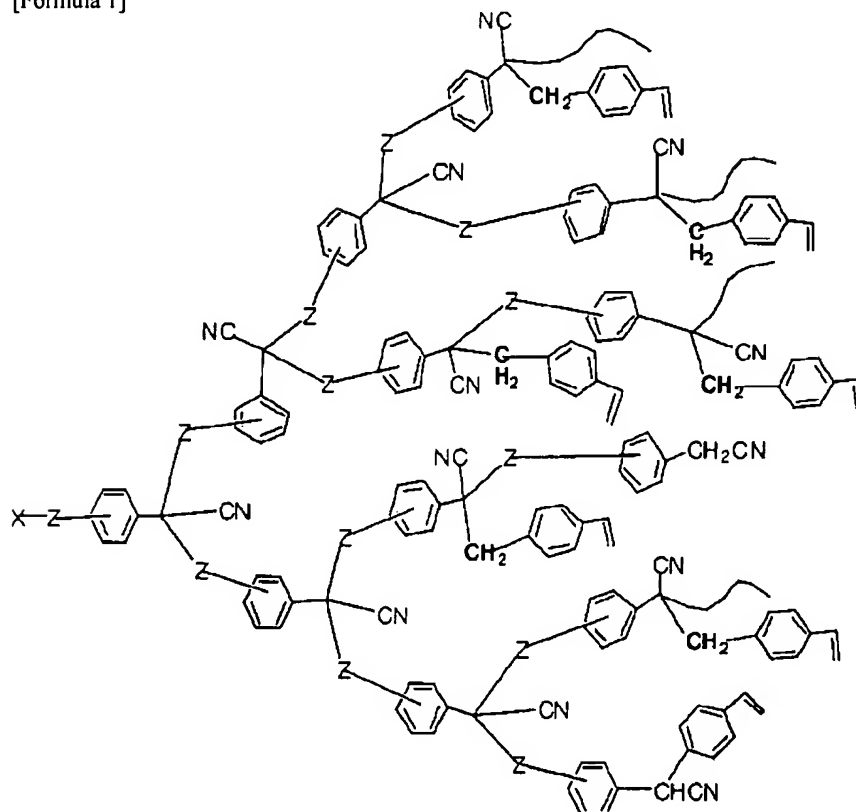
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CLAIMS

[Claim(s)]

[Claim 1] General formula (I)

[Formula 1]



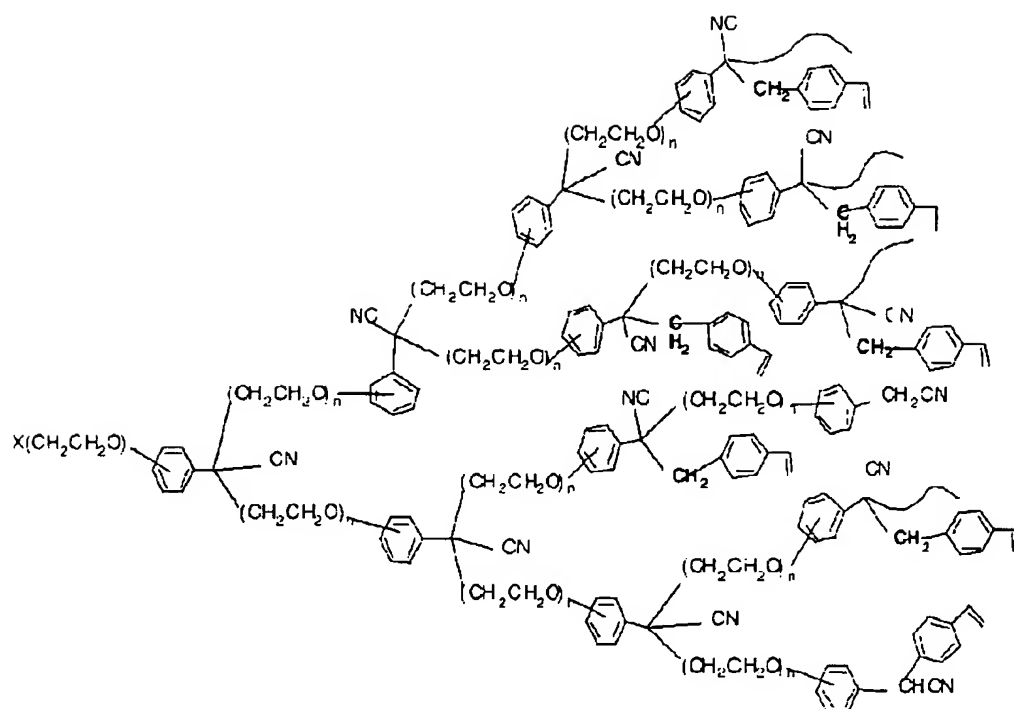
X is a halogen atom, three p-CH₃PhSO(s), or a hydroxyl group among [type, and Z is -(OCH₂CH₂)_n, -O(CH₂)_n, or -OCH₂Ph (n is the integer of 1-12). the end oxygen atom is combined at least with o-, m-, and p- of the benzene ring -- radical copolymerization of the multi-branch-type multi-styrene macro monomer expressed with] and the olefin compound is carried out -- The manufacturing method of the copolymer of the multi-branch-type multi-styrene macro monomer and olefins by which the olefin compound was combined with the double bond part of styrene residue.

[Claim 2] The manufacturing method of the copolymer of the multi-branch-type multi-styrene macro monomer and olefin compound according to claim 1 whose olefin compounds are one or more sorts of polymerization nature monomers chosen from styrene, methacrylate, acrylate, acrylamides, and vinylpyridines.

[Claim 3] The copolymer of the multi-branch-type multi-styrene macro monomer and olefins which are manufactured according to a manufacturing method according to claim 1 or 2.

[Claim 4] The general formula which is manufactured according to a manufacturing method according to claim 1 or 2 and whose Z is -(OCH₂CH₂)_n (II)

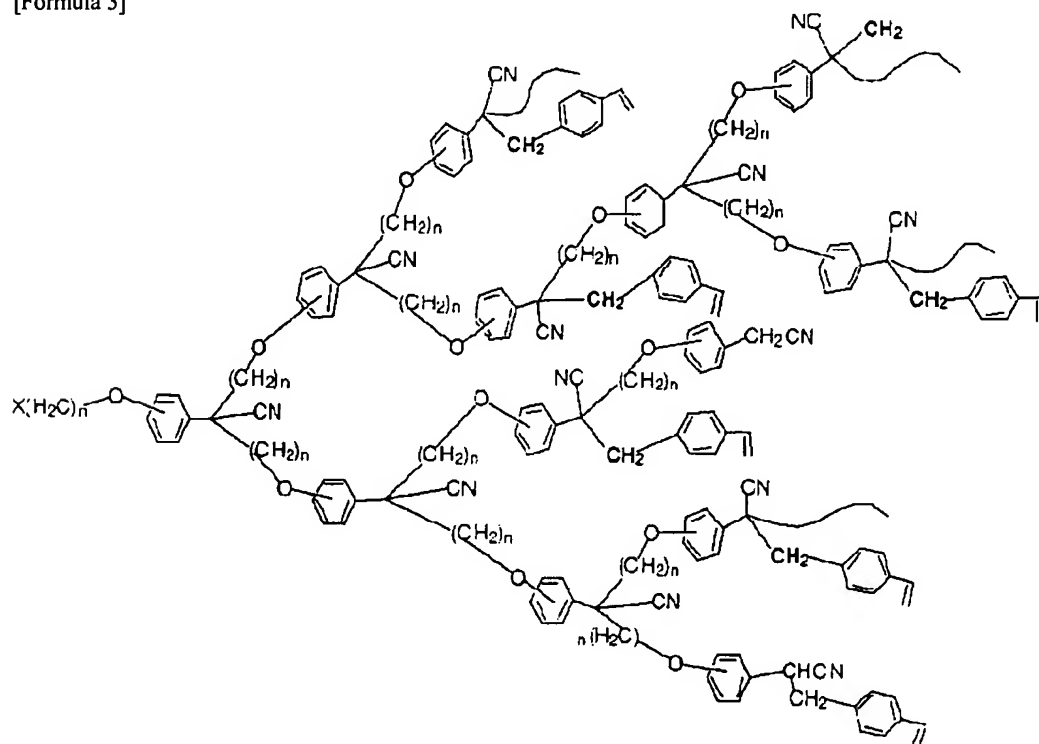
[Formula 2]



(-- the copolymer of the multi-branch-type multi-styrene macro monomer and olefin compound by which n is expressed with integer) of 1-10 here.

[Claim 5] The general formula which is manufactured according to a manufacturing method according to claim 1 or 2 and whose Z is $-O(CH_2)_n$ (III)

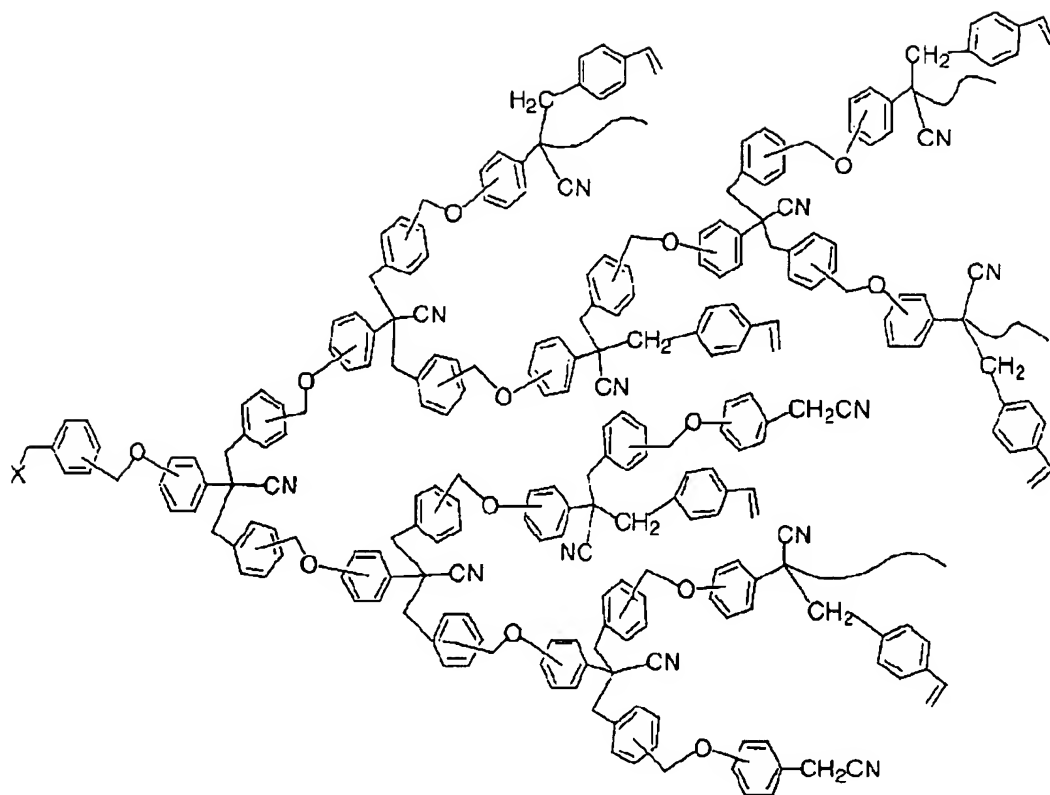
[Formula 3]



(-- the copolymer of the multi-branch-type multi-styrene macro monomer and olefin compound by which n is expressed with integer) of 2-12 here.

[Claim 6] The general formula which is manufactured according to a manufacturing method according to claim 1 or 2 and whose Z is $-OCH_2Ph$ (IV)

[Formula 4]



(-- the copolymer of the multi-branch-type multi-styrene macro monomer and olefin compound by which n is expressed with integer) of 1-6 here.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the copolymer with which the hybrid of the letter structure polymer of many branching was carried out to the liner polymer structure by the copolymerization reaction of a many branching nature multi-styrene macro monomer and an olefin compound (olefin system monomer), and its manufacture approach. namely, the line of the copolymer of this invention -- a part is a polymer which has the repeat unit which consists of olefins monomers, and the letter part of branching consists of a polycondensation system polymer which consisted of random branching structures. the line in this invention -- the letter hybrid mold copolymer of - branching is useful to the invention of new macromolecule resin and polymeric materials.

[0002]

[Description of the Prior Art] Although copolymerization of a macro monomer and an olefins monomer is useful to various macromolecule construction and the development research about the manufacturing technology of that is also developed briskly The monomer structure of a piece is introduced into the end of a straight chain mold macromolecule, and the most the conventional macro monomer at the polymerization reaction using it There are no liner polymer structure and change which the copolymerization reaction of the olefin monomers from which the usual structure differs gives, and the copolymer which grew up to be a line fundamentally is formed. Therefore, although the linear block copolymer with which a macro monomer is concerned, a graft copolymer, and a core-corona mold macromolecule particle can be manufactured in a Prior art, the example of a copolymer which has the branching structure which spreads variably is rare.

[0003] From the copolymerization reaction with the olefins monomer using the macro monomer which styrene residue combined with the end of polystyrene, the copolymer of structure with which the polystyrene side chain hung down from the polystyrene principal chain, or a principal chain is the copolymerization frame of polystyrene-polymethacrylate, and the manufacture approach of the copolymer of structure that polystyrene hung down from the side chain is shown in polymer (Polymer)"35 volume, 2205 pages, 1994}, and {"macro leakage-at-bulb KYURUSU (Macromolecules)" 22 volume, 1546 pages and 1989}.

[0004] Moreover, the manufacture approach of the copolymer of the macro monomer and olefins by which acrylate residue was introduced into the polystyrene end is indicated in macro leakage-at-bulb KYURUSU (Macromolecules), 22 volumes, 2869 pages, and 1989.

Moreover, as for the principal chain by the copolymerization reaction of the macro monomer and styrene with which styrene residue was introduced into the end of polyethylene oxide, the manufacture approach of the copolymer of structure that polyethylene oxide hung down from styrene and side-chain structure is shown in macro leakage-at-bulb KYURUSU (Macromolecules), 30 volumes, 2811 pages, and 1997.

[0005] On the other hand, the copolymer using the branching nature macro monomer of a non-straight chain mold captures the spotlight recently. For example, the method of manufacturing the polymer which branched polymer structure combined with the side chain by making the FAKARU point of a branching nature macromolecule carry out copolymerization of the macro monomer which has the monomer residue of a piece to homopolymerization or other olefins monomers is indicated in a journal, OBU, a polymer, Science, a PERT A: polymer, chemistry (J.Polym.Sci.Part A:Polym.Chem.), 36 volumes, 955 pages, and 1998.

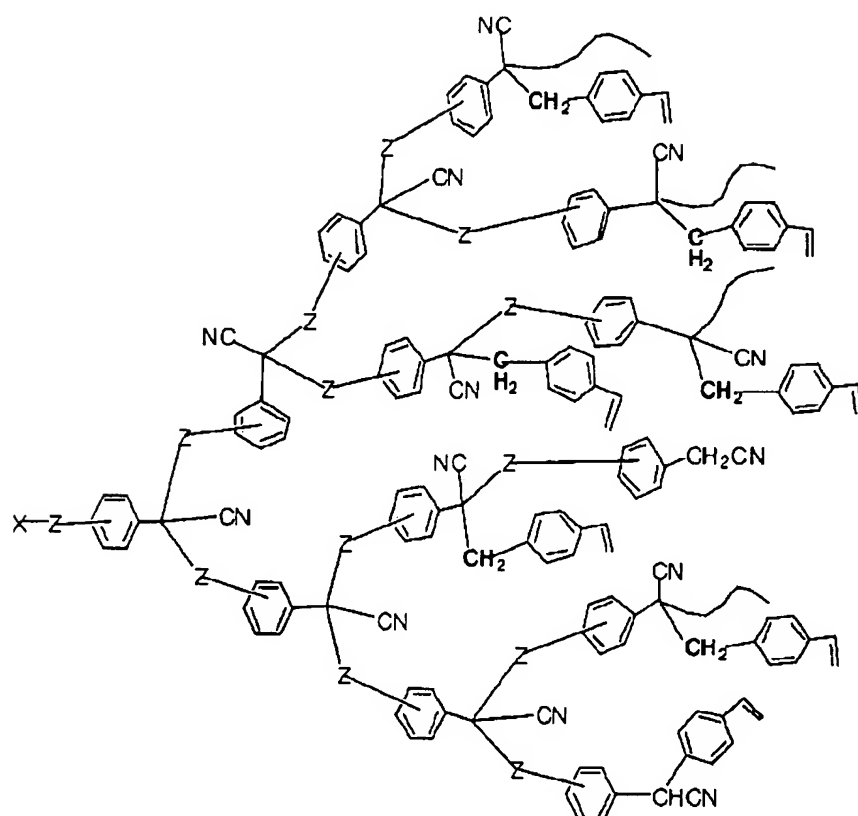
[0006]

[Problem(s) to be Solved by the Invention] The technical problem which this invention tends to solve is to provide a solvent with the new copolymer of a meltable styrene system macro monomer and a meltable olefinic compound, and its manufacturing method, having high molecular weight.

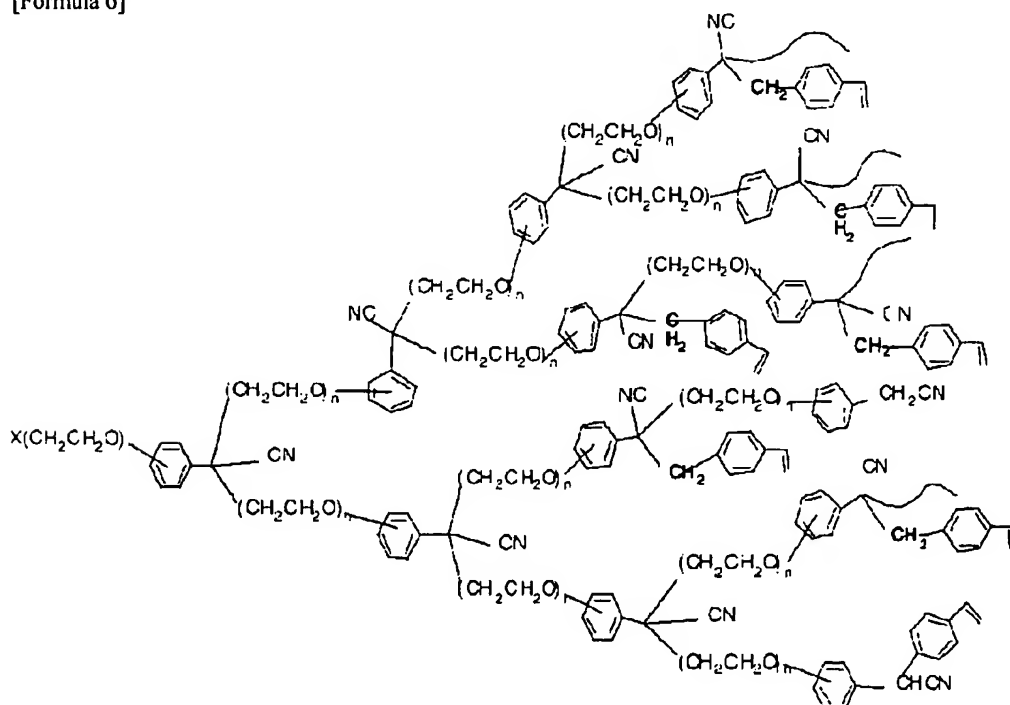
[0007]

[Means for Solving the Problem] It came to complete a header and this invention for the ability of a meltable new copolymer to be manufactured to a solvent, having high molecular weight by carrying out copolymerization of the multi-branch-type multi-styrene macro monomer to the Ole Phi system monomer, as a result of inquiring wholeheartedly, in order to solve the above-mentioned technical problem. That is, this invention is (1) general formula (1).

[Formula 5]

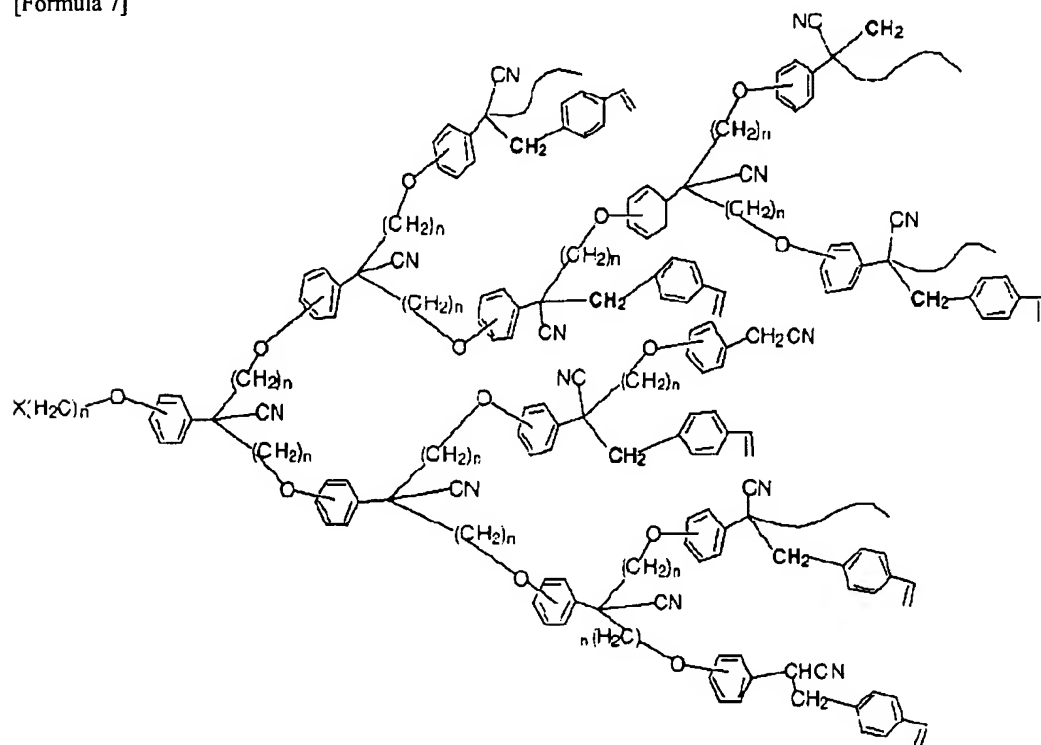


X is a halogen atom, three p-CH₃PhSO(s), or a hydroxyl group among [type, and Z is -(OCH₂CH₂)_n, -O(CH₂)_n, or -OCH₂Ph (n is the integer of 1-12). the end oxygen atom is combined at least with o-, m-, and p- of the benzene ring -- radical copolymerization of the multi-branch-type multi-styrene macro monomer expressed with] and the olefin compound is carried out -- The manufacturing method of the copolymer of the multi-branch-type multi-styrene macro monomer and olefins by which the olefin compound was combined with the double bond part of styrene residue, and [0008] (2) The manufacturing method of the copolymer of the multi-branch-type multi-styrene macro monomer given in (1) and olefin compound whose olefin compounds are one or more sorts of polymerization nature monomers chosen from styrene, methacrylate, acrylate, acrylamides, and vinylpyridines, and [0009] (3) The copolymer of the multi-branch-type multi-styrene macro monomer and olefins which are manufactured according to above (1) or a manufacturing method given in (2), and [0010] (4) The general formula which is manufactured according to above (1) or a manufacturing method given in (2) and whose Z is -(OCH₂CH₂)_n (II)
[Formula 6]



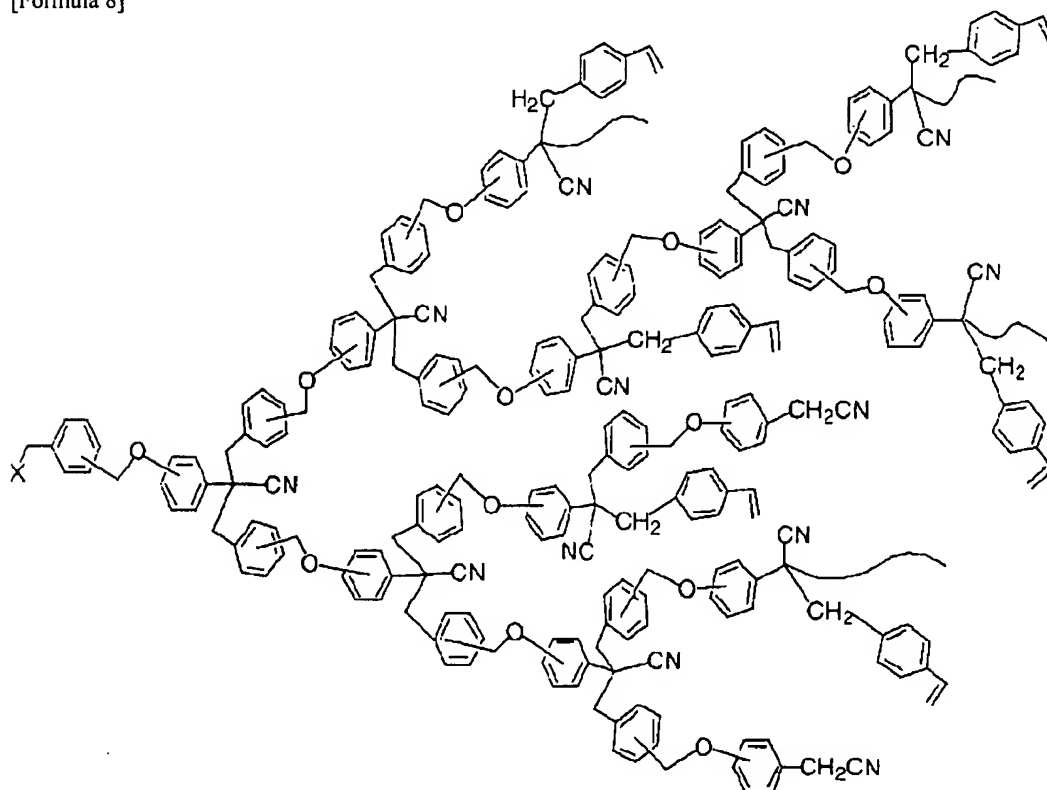
(-- the copolymer of the multi-branch-type multi-styrene macro monomer and olefin compound by which n is expressed with integer) of 1-10 here, and [0011] (5) The general formula which is manufactured according to above (1) or a manufacturing method given in (2) and whose Z is $-\text{O}(\text{CH}_2)_n$ (III)

[Formula 7]



(-- the copolymer of the multi-branch-type multi-styrene macro monomer and olefin compound by which n is expressed with integer) of 2-12 here, and [0012] (6) The general formula which is manufactured according to above (1) or a manufacturing method given in (2) and whose Z is $-\text{OCH}_2\text{Ph}$ (IV)

[Formula 8]



(-- n contains the copolymer of the multi-branch-type multi-styrene macro monomer expressed with integer) of 1-6, and an olefin compound here.

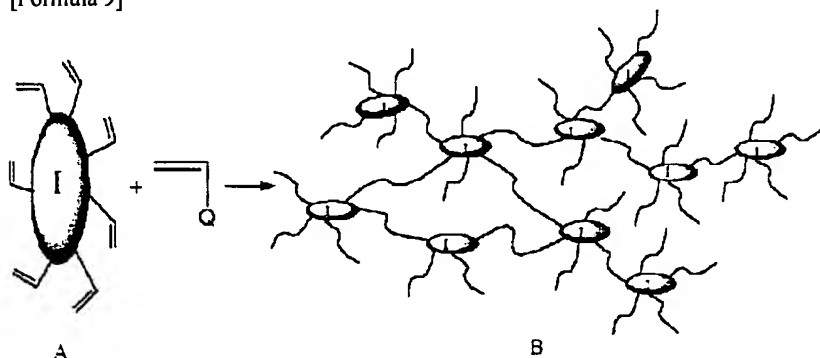
[0013]

[Embodiment of the Invention] Since the multi-branch-type multi-styrene macro monomer used by this invention combines much monomer residue at random in branching structure unlike the macro monomer which has only one conventional olefin residue, in the polymerization with which it is concerned, the multi-branch-type multi-styrene macro monomer itself will be equipped with the usual low-molecular multi-functional-group mold cross linking agent-function.

[0014] It is known well that a low-molecular cross linking agent monomer will give the insoluble polymer gelled usually in three dimensions. However, from the three-dimensional structure element, the multi-branch-type multi-styrene macro monomer which combined with the polymer of branching structure the styrene residue of a large number used by this invention is the copolymerization reaction of other olefins, and can be stopped to the two-dimensional bridge formation without gelation by control of the polymerization. The two-dimensional structure of cross linkage is formation of the network structure which made the multi-styrene macro monomer the island field, and the structure of an "island-suspension bridge" mold. ** 9 showed this typically.

[0015]

[Formula 9]



[0016] (A expresses a general formula (I) among a formula, and Q is a substituent which has the double bond and conjugated double bond of an olefin compound)

[0017] the copolymer (letter of following and branching - a line -- there is a hybrid polymer or a thing only called hybrid copolymer) of the multi-branch-type multi-styrene macro monomer and olefins which are obtained by this invention has the structure of a star type polymer where many linear polymers were combined with one multi-branching structure polymer. Furthermore, the hybrid copolymer of this invention has the structure of a two-dimensional network mold where some many branching nature polymers were connected by much liner polymer.

[0018] Moreover, at the copolymerization reaction in this invention, the blend mold polymer with which the above-mentioned star type polymer or a network mold polymer, and simple liner polymer were mixed can also be given. Furthermore, at the copolymerization reaction in this invention, the three dimensions network mold polymer resulting from bridge formation of a multi-styrene mold branching macro monomer can also be given.

[0019] the line in this invention -- generally the letter hybrid copolymer of - branching can be manufactured by the following approaches. An olefin compound (olefin system monomer) and a solvent are added to the container containing the multi-branch-type multi-styrene macro monomer expressed with a general formula (I), it fully agitates, and these are dissolved completely. A polymerization initiator is added to this mixed solution, and it is made to react, heating a reaction solution to constant temperature and carrying out fixed time amount churning. the line into which the branching macro monomer was introduced by carrying out a ** exception, accepting the need, and washing and drying a copolymer with a solvent after adding the poor solvent to reaction mixed liquor and settling a copolymer after reaction termination -- the letter hybrid copolymer of - branching can be obtained.

[0020] The multi-branch-type multi-styrene macro monomer expressed with the general formula (I) of this invention can be manufactured according to the manufacture approach indicated by JP,2000-128848,A.

[0021] As a multi-branch-type multi-styrene macro monomer to be used, z is n(CH₂CH₂O)- also in the multi-branch-type multi-styrene macro monomer expressed with a general formula (I), as for the oxygen atom of n(CH₂CH₂O)-, what is combined at least with o-, m-, or p- of the benzene ring is desirable, and especially its thing that the oxygen atom has combined at least with p- is desirable. Furthermore (CH₂CH₂O), n of n- has the desirable thing of 1 to 10, and the numeric value of especially the thing of 2 or 3 is desirable.

[0022] As a multi-branch-type multi-styrene macro monomer to be used, z is -O(CH₂) n also in the multi-branch-type multi-styrene macro monomer expressed with a general formula (III), as for the oxygen atom, what is combined at least with o-, m-, or p- of the benzene ring is desirable, and especially its thing that the oxygen atom has combined at least with p- is desirable. Furthermore, n of -O(CH₂) n has the desirable thing of 2 to 12, and the numeric value of especially the thing of 4 to 8 is desirable.

[0023] As a multi-branch-type multi-styrene macro monomer to be used, as for the oxygen atom of -OCH₂Ph, what is combined at least with o-, m-, or p- of the benzene ring is desirable also in the multi-branch-type multi-styrene macro monomer expressed with a general formula (IV), and especially the thing that the oxygen atom has combined at least with p- is desirable.

[0024] As an olefin compound used for the manufacture reaction of the above-mentioned copolymer, there are a styrene system compound, for example, styrene, 2-chloro methyl styrene, 3-chloro methyl styrene, 4-chloro methyl styrene, p-methoxy styrene, p-vinyl benzoic acid, a p-vinyl phenyl sulfonic acid, etc., and it is [0025]. Next, as a vinylpyridine compound, p-vinylpyridine and o-vinylpyridines are mentioned and it is methyl methacrylate, ethyl methacrylate, butyl methacrylate, t-butyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 2-hydroxyethyl methacrylate, 2-dimethylaminoethyl methacrylate, and [0026] as a methacrylate system compound, for example. As an acrylate system compound, methyl acrylate, ethyl acrylate, butyl acrylate, t-butyl acrylate, hexyl acrylate, cyclohexyl acrylate, benzyl acrylate, 2-hydroxyethyl acrylate, 2-dimethylamino ethyl acrylate, etc. are mentioned, for example.

[0027] Moreover, as an acrylamide compound which is an olefin compound used for the manufacture reaction of the copolymer of this

invention, acrylamide, N,N-dimethylacrylamide, N, and N-diethyl acrylamide, N-isopropyl acrylamide, etc. are mentioned, for example. [0028] In the copolymerization reaction of this invention, different polymerization methods, such as bulk polymerization in those without a solvent, solution polymerization under solvent existence, or emulsion polymerization under existence of an alcohols solvent, are applicable.

[0029] As a solvent which can be used for the copolymerization reaction of this invention, a tetrahydrofuran, an acetonitrile, benzene, toluene, a chlorobenzene, a dichlorobenzene, an anisole, cyanobenzene, dimethyl formamide, N,N-dimethylacetamide, a methyl ethyl ketone, etc. are mentioned. Furthermore, as an alcohols solvent used for emulsion polymerization, fatty alcohol, such as propanol, a butanol, a pentanol, and a hexanol, is mentioned.

[0030] Although the temperature of the copolymerization reaction of this invention changes with olefin compounds, solvents, etc. to be used, generally it can be set as the range from a room temperature to 130 degrees C, is desirable, and is more desirable. [of the range which is 60-100 degrees C] [of the reaction temperature of 40-100 degrees C]

[0031] As for reaction time, it is desirable to set up the reaction time with the class of initiator, the class of olefin monomer, and reaction temperature for 1 to 24 hours, although it is enough in the range. Furthermore, as for a setup of reaction time, it is desirable to set up to compensate for molecular weight control of the copolymer obtained.

[0032] It is desirable to use a polymerization initiator for the copolymerization reaction of this invention. Although these polymerization initiators are fundamentally limited to a radical polymerization initiator, both the radical polymerization initiator of well-known common use and other living radical polymerization initiators can be used for them.

[0033] As a usual radical polymerization initiator, 2 and 2-azobis isobutyl nitril, 2, and 2-azobis (cyclohexane-1-carbonitrile), 2, and 2-azobis (2-methyl butyronitrile) 2, 2-azobis (2,4-dimethylvaleronitrile), 2, and 2-azobis [2-(hydroxymethyl) propionitrile], potassium peroxydisulfate, a ammonium peroxydisulfate, dibenzoyl peroxide, etc. are mentioned.

[0034] Moreover, as a sulfonic-acid chloride compound, benzenesulfonic acid chloride, p-methylbenzene sulfonic-acid chloride, p-methoxybenzene sulfonic-acid chloride, p-fluorobenzene sulfonic-acid chloride, etc. are mentioned.

[0035] It is the living radical polymerization initiator which makes a catalyst an initiator molecule, and transition-metals haloid salt and a bipyridine complex as a living radical polymerization initiator for the organic halogen or sulfonic-acid chloride which is an atomic migration radical polymerization system, for example. As an organic halogenated compound, chloro methylbenzene, bromomethyl benzene, 1-chloroethylbenzene, 1-BUOMO ethylbenzene, 1-iodine ethylbenzene, 1-BUOMO ethyl propionate ester, etc. are mentioned.

[0036] as transition-metals haloid salt -- a cuprous chloride and bromination -- the first copper, a cuprous iodide, ferric chloride, a nickel chloride, etc. are mentioned. As bipyridines, 2, a 2'-bipyridine, 4, the 4'-dimethyl -2, a 2'-bipyridine, etc. are mentioned.

[0037] moreover, the line which combined the halogen atom, for example, a bromine, with the end as a macro initiator -- the polymethacrylate which combined the bromine with polystyrene or an end is mentioned. By the polymerization system using a macro initiator, for example, the styrene residue in a macro initiator and a macro monomer is made to react, the active spot used as a growth end combines with the frame of a macro monomer, an olefin monomer is added to it, and the star type polymer which used as the arm the chain of the olefin by which the polymerization was carried out to the chain of a macro initiator the core [a macro monomer] by continuing a polymerization is obtained.

[0038] Furthermore, it is the living polymerization initiator which combined the dithio ester chain transfer agent with the usual radical polymerization initiator molecule which is an reversible addition-fragmentation chain transition polymerization system as a living radical polymerization initiator, for example. As a chain transfer agent, a dithio ester compound is mentioned like benzylbenzene dithio ester, dimethylphenyl methylbenzene dithio ester, and benzyl acetic-acid dithio ester.

[0039] Although the preparation rate of the multi-styrene macro monomer and olefins monomer which are used for a copolymerization reaction has and computes the mole ratio of the styrene residue in a multi-styrene macro monomer, and an olefin monomer, it is desirable that the range of the mole ratio is 0.1 / 100 - 20/100, the ratio of the range of 0.1 / 100 - 10/100 is still more desirable, and especially its range of 0.3 / 100 - 5/100 is desirable.

[0040] letter of "island-suspension bridge" mold branching - which the gelation reaction did not occur but was excellent in solubility with the copolymerization reaction in the mole ratio of the styrene residue in the multi-styrene macro monomer in the above-mentioned range, and an olefin monomer -- a line -- a hybrid copolymer is obtained. If it puts in another way and the mole ratio of a multi-styrene macro monomer will exceed 20/100, it will be easy to generate gelation and sufficient effectiveness of copolymerization will be it hard to be acquired to be less than 0.1/100.

[0041] the copolymer obtained from the radical copolymerization reaction of the olefins using the letter of branching multi-styrene macro monomer of this invention -- letter of branching - of an "island-suspension bridge" mold -- a line -- it is presumed that it is constituted by hybrid construction. molecular weight with the very expensive copolymer of this invention -- concrete -- average weight molecular weight - 100,000-1 million -- desirable -- 200,000-700,000 -- it has a meltable property to an organic solvent, having 300,000-500,000 still more preferably.

[0042] These organic solvents are a tetrahydrofuran, an acetonitrile, benzene, toluene, a chlorobenzene, a dichlorobenzene, an anisole, cyanobenzene, dimethyl formamide, N,N-dimethylacetamide, a methyl ethyl ketone, etc. Because of this property, the copolymer of this invention is useful as new various functions-polymeric materials which have advanced reinforcement and still stronger ligament nature while it has the outstanding workability.

[0043]

[Example] High performance chromatography (HLC[by TOSOH CORP.]- 8020), RI detector, TSKgel 2000xl+3000Hxl+5000 Hxl+guardcolumnHxl-H, solvent THF rate-of-flow: 1.0 ml/min, temperature control: (GPC measuring method) It measured at 40 degrees C.

[0044] (Example 1 of reference) 4-(4-chloro methyl benzoRUOKI) phenylacetonitrile 2.46g, 4-chloro methyl styrene 0.67g, and dimethyl sulfoxide 200ml were added to the eggplant mold flask of 1000ml of [composition of macro monomer (cable address: St-BPA-MM -1) of benzoRUOKI phenylacetonitrile skeletal system which has styrene residue] MAG stirring *****. Stirring this mixed solution by the stirrer, 20ml of 50% of hydroxylation NATORIRUMU water solutions was added to once, and that mixed liquor was stirred at 30 degrees C for 1 hour. Then, KUENCHI [400ml of distilled water was added and / the reaction].

[0045] After having dropped 10% of hydrochloric-acid water solution, neutralizing the solution and leaving it in the state of that neutralization for about 1 hour, stirring in this water solution, suction filtration was carried out and the precipitating polymer was repeatedly washed in order of distilled water and METANORU 3 times. tetrahydrofuran after drying obtained polymer at room temperature

25ml -- dissolving -- the solution -- methanol 250ml -- it flowed into inside and the polymer was settled. Put the polymer into the desiccator after suction filtration, decompressed with the vacuum pump, it was made to dry under a vacuum for 24 hours, and branch-type multi-styrene macro monomer (it abbreviates to St-BPA-MM -1 hereafter.) 2.56g was obtained. (96.2% of yield)

[0046] The number average molecular weight measured using GPC (gel permeation chromatography) of the polymer (St-BPA-MM -1) obtained in the example 1 of reference was 4400, and molecular weight distribution were 1.48. Moreover, when the integral ratio of the methylene proton (4.4-4.6 ppm) of the polymer FAKARU point and the proton (4.8-5.3 ppm) of the methylene oxide in a polymer frame was calculated from the measurement result of ¹H-NMR, the number of repeats of the phenylacetonitrile in a polymer, i.e., a number average degree of polymerization, was 15. Furthermore, the mol presentation ratio of the phenylacetonitrile in [the measurement result of ¹H-NMR to] a polymer and styrene was 72:28. this mol -- a presentation ratio -- mol brewing -- the numeric value of 67 to 33 of a ratio is approached.

[0047] (Example 2 of reference) In the example 1 of [composition of macro monomer (cable address: St-BPA-MM -2) of benzoRUOKI phenylacetonitrile skeletal system which has styrene residue] reference, branch-type multi-styrene macro monomer (it abbreviates to St-BPA-MM -2 hereafter.) 2.92g was obtained like the example 1 except having used 4-chloro methyl styrene 1.34g. [(91.8% of yield) 0048] The number average molecular weight in GPC of a polymer (St-BPA-MM -2) was 5300, and molecular weight distribution were 1.26. Moreover, when the integral ratio of the methylene proton (4.4-4.6 ppm) of the polymer FAKARU point and the proton (4.8-5.3 ppm) of the methylene oxide in a polymer was calculated from the measurement result of ¹H-NMR, the number of repeats of the phenylacetonitrile which forms a polymer frame, i.e., a number average degree of polymerization, was 12. Furthermore, the mol presentation ratio of the phenylacetonitrile in [the measurement result of ¹H-NMR to] a polymer and styrene was 60:40. this mol -- a presentation ratio -- mol brewing -- the numeric value of 50 to 50 of a ratio is approached.

[0049] The example 1 of reference and the example 2 of reference show that the content of the styrene residue of a macro monomer is easily controllable by changing the brewing rate of the phenylacetonitrile in a polymerization reaction, and chloro methylene styrene.

[0050] (Example 3 of reference) [Composition of macro monomer (cable address: I2-MS) of alkoxy phenylacetonitrile skeletal system which has styrene residue] 4-(2-(2-bromoethoxy)-ethoxy) phenylacetonitrile (30 weight sections) It dissolved in DMSO (1000 weight sections), and 60% of sodium-hydroxide water solution (80 weight sections) was added, having set the temperature of a solution as 30 degrees C, and agitating it violently. After agitating the mixture for 1.6 hours, 4-chloro methyl styrene of 60 weight sections was added, and churning was continued at the same temperature for 4 hours. Then, reaction mixture was added to a lot of distilled water, and the hydrochloric-acid water solution was dropped at the mixed liquor 10% (pH=4).

[0051] The precipitate after standing was filtered and distilled water washed the solid-state. The obtained solid-state was dissolved in the methylene chloride after room temperature desiccation, the petroleum ether was filled with the solution, and the polymer was made to reprecipitate. Macro monomer I2-MS into which styrene residue was introduced was obtained through suction filtration and a vacuum drying. Yield (85%). The weight average molecular weight in GPC was 5180, the molecular weight distribution was 2.17, and the amount of installation of styrene was 3.5 mmol/g.

[0052] Hereafter, n which can mainly be expressed with a general formula (I) is 2, an oxygen atom is association like p-of the benzene ring, weight average molecular weight is 5180, a molecular weight distribution is 2.17, and styrene residue explains this invention to a detail further using the example using the multi-styrene macro monomer (abbreviation: describe it as I2-MS) which is 3.5 mmol/g.

[0053] (Example 1) The nitrogen purge of the eggplant mold flask equipped with [composition of copolymer (cable address--I2-MS-St -1) of multi-branch-type multi-styrene macro monomer and olefins by copolymerization of I2-MS and styrene] MAG stirring child is carried out, and it is styrene of I2-MS of the 0.3 weight section, the azobis isobutyl nitril of the 1.09 weight sections, and the 109 weight sections to it. The toluene of 12 weight sections was added and the mixed solution was prepared. Stirring this mixed solution by the stirrer, it heated with the 100-degree C oil bath, and was made to react for 15 hours.

[0054] When polymerization reaction mixture was measured in ¹H NMR, the invert ratio of a styrene monomer was 97%. This polymer was settled in a lot of hexanes, and suction filtration washed the polymer solid. After drying a polymer at a room temperature, under the vacuum, it was made to dry for 24 hours and 60 degree C of polymer P-I2-MS-St -1 were obtained with 89% of yield. The weight average molecular weight in GPC of a copolymer (P-I2-MS-St -1) was 446000, and molecular weight distribution were 14.

[0055] (Example 1 of a comparison) The weight average molecular weight of the polystyrene obtained without the macro monomer by homopolymerization of only styrene was 90000 under the condition same as a control experiment as the same preparation as an example 1, and molecular weight distribution were 3.5.

[0056] (Example 2) The nitrogen purge of the eggplant mold flask equipped with [composition of copolymer (cable address--I2-MS-St -2) of multi-branch-type multi-styrene macro monomer and olefins by copolymerization of I2-MS and styrene] MAG stirring child was carried out, the azobis isobutyl nitril of I2-MS of the 2.0 weight sections and the 0.55 weight sections, the styrene of the 54.6 weight sections, and the toluene of the 54.6 weight sections were added, and the mixed solution was prepared. Stirring this mixed solution by the stirrer, it heated with the 100-degree C oil bath, and was made to react for 1 hour.

[0057] When polymerization reaction mixture was measured in ¹H NMR, the invert ratio of a styrene monomer was 47%. This polymer was settled in a lot of hexanes, and suction filtration washed the copolymer solid. After drying a copolymer at a room temperature, under the vacuum, it was made to dry for 24 hours and 60 degree C of copolymer P-I2-MS-St -2 were obtained with 40% of yield. The weight average molecular weight in GPC of a copolymer (P-I2-MS-St -2) was 258000, and molecular weight distribution were 9.9.

[0058] (Example 2 of a comparison) The weight average molecular weight of the polystyrene which the invert ratio of a monomer is 50% in the case of homopolymerization of only styrene, and was obtained without the macro monomer was 47700 under the condition same as a control experiment as the same preparation as an example 2, and molecular weight distribution were 2.9.

[0059] As for weight average molecular weight, as for the homopolymer of styrene without the macro monomer in conditions with the same copolymer obtained by copolymerization of styrene and a multi-styrene macro monomer, from the result of an example 1 and an example 2, more than quintuple shows having been extended. That is, weight average molecular weight can manufacture hundreds of thousands or more copolymers easily by addition of few letter of branching multi-styrene macro monomers.

[0060] (Example 3) In the eggplant mold flask equipped with [composition of copolymer (cable address--I2-MS-St -4) by atomic migration radical copolymerization of I2-MS and styrene] MAG stirring child 2 of the copper bromide of I2-MS of the 6.0 weight sections, 1-BUROMO ethylbenzene of the 3.6 weight sections, and the 2.7 weight sections and the 9.0 weight sections, 2-bipyridine, the styrene of 66 weight sections, and the toluene of the 110 weight sections were added, and the mixed solution was prepared. It stirred for 24 hours, heating with a 100-degree C oil bath, after carrying out bubbling of this solution by argon gas for 30 minutes.

[0061] The invert ratio of the styrene in a reaction termination time was 100%. After adding little THF to reaction mixture, the solution was poured out into a lot of methanols, and the polymer was settled. The polymer solid was dried at the room temperature after washing by suction filtration, further, under the vacuum, it was made to dry for 24 hours and 60 degree C of polymer P-I2-MS-St -3 were obtained with yield 100%. The weight average molecular weight in GPC of a copolymer (P-I2-MS-St -3) was 171000, and molecular weight distribution were 5.7.

[0062] (Example 3 of a comparison) The weight average molecular weight of the polystyrene which the invert ratio of a monomer is 100% in the case of homopolymerization of only styrene, and was obtained without the macro monomer was 6200 under the condition same as a control experiment as the same preparation as an example 3, and molecular weight distribution were 1.2.

[0063] As the mole ratio (1 to 33) of an initiator and a styrene monomer, from the description of the living radical polymerization, the molecular weight of a polymer stopped at about 5000 order, and it was more nearly inelastic than it in it with the example 3 of a comparison. In spite of the same mole ratio (1 to 33), the weight average molecular weight of the obtained hybrid polymer went up by the example 3 to 170,000 or more by slight existence of a multi-styrene macro monomer. Structure from which the "island" and the "island" were connected with the suspension bridge to the polymer obtained in the example 3 can be presumed. namely, letter of branching - a line - it is formation of a hybrid polymer.

[0064] (Example 5) [-- the line of end bromine association of I2-MS and styrene -- letter of branching - by the polystyrene initiator -- a line -- synthetic] [0065] of a hybrid polymer (cable address--I2-MS-St -4) [-- the line of end bromine association -- the styrene of 2 of the

copper bromide of 1-BUROMO ethylbenzene of the 1.14 weight sections and the 0.86 weight sections and the 2.81 weight sections, 2-bipyridine, and the 21.8 weight sections was added to the eggplant mold flask equipped with synthetic] MAG stirring child of polystyrene (abbreviation-S-Br), and the mixed solution was prepared. It stirred for 15 hours, heating with a 100-degree C oil bath, after carrying out bubbling of this solution by argon gas for 30 minutes. The invert ratio of the styrene in a reaction termination time was 90%.

[0066] After adding little THF to reaction mixture, the solution was poured out into a lot of methanols, and the polymer was settled. The polymer solid was dried at the room temperature after washing by suction filtration, further, under the vacuum, it was made to dry for 24 hours and 60 degrees C (abbreviation-S-Br) of end star's picture tie-like polystyrene were obtained with yield 80%. The weight average molecular weight in GPC of PS-Br was 8300, and molecular weight distribution were 1.4.

[0067] The toluene of 2 of PS-Br of I2-MS of the 1.0 weight sections and 10 weight sections, the copper bromide of the 0.45 weight sections, and the 1.5 weight sections, 2-bipyridine, and the 110 weight sections was added to the eggplant mold flask equipped with the [two-step, multi-styrene macro monomer [which makes PS-Br an initiator], and styrene, polymerization] MAG stirring child, and the mixed solution was prepared. It stirred for 15 hours, heating with a 100-degrees C oil bath, after carrying out bubbling of this solution by argon gas for 30 minutes. The weight average molecular weight of the polymer in GPC in this time was 14400, and molecular weight distribution were 1.6. The styrene 6.55 weight section was further added to this polymerization reaction mixture, and it agitated at 100 degrees C for 24 hours.

[0068] After adding little THF to reaction mixture, the solution was poured out into a lot of methanols, and the polymer was settled. The polymer solid was dried at the room temperature after washing by suction filtration, further, under the vacuum, it was made to dry for 24 hours and 60 degree C of polymer P-I2-MS-St -4 were obtained with yield 80%. The weight average molecular weight in GPC of a polymer (P-I2-MS-St -4) was 105000, and molecular weight distribution were 3.6.

[0069] (Example 6) [-- letter of branching - in the living radical copolymerization system of I2-MS and styrene -- a line -- related] [0070] of the formation and time amount of a hybrid polymer 2 of the copper bromide of I2-MS of the 3.0 weight sections, 1-BUROMO ethylbenzene of the 1.8 weight sections, and the 1.38 weight sections and the 4.5 weight sections, 2-bipyridine, the styrene of 33 weight sections, and the toluene of 55 weight sections were added to the eggplant mold flask equipped with the magnetic stirring child, and the mixed solution was prepared. Agitating with the oil bath heated at 100 degrees C, after carrying out bubbling of this solution by argon gas for 30 minutes, some sample was taken out in the syringe for every fixed time amount, and GPC measurement of that sample and 1H NMR measurement were performed.

[0071] (Example 4 of a comparison) As a control experiment, the styrene of 2 of the copper bromide of 1-BUROMO ethylbenzene of the 1.8 weight sections and the 1.38 weight sections and the 4.5 weight sections, 2-bipyridine, and 33 weight sections was added to the eggplant mold flask equipped with the magnetic stirring child, and the mixed solution was prepared. After carrying out bubbling of this solution by argon gas for 30 minutes, when it agitated for 4 hours and the degree of the polymerization in that time was checked by GPC and 1H NMR measurement, agitating with a 100-degree C oil bath, the invert ratio of a monomer was 93%, weight average molecular weight was 5000, and molecular weight distribution were 1.26.

[0072] The mole ratio of 1-BUROMO ethylbenzene both the above-mentioned experiments of whose are initiators, and the styrene which is a monomer is 1 to 33. Therefore, the molecular weight of the linear polystyrene by this ratio is logically impossible for exceeding 10,000.

[0073] the GPC chart of the copolymer for every polymerization time amount of an example 6, and the line of a comparative study -- the result of polystyrene is shown in drawing 1 . the top curve -- the styrene homopolymerization system as an example of a comparison -- it is -- the line in the time of reaction 4 hours, and 93% of invert ratios -- it is the GPC chart of polystyrene.

[0074] The less than second is a GPC chart in the time of reaction 2 hours of the copolymerization system of an example 6 (25% of invert ratios), 3 hours, 4 hours (49% of invert ratios), 5 hours (55% of invert ratios), 5.5 hours, 6 hours (58% of invert ratios), 6.5 hours, 7 hours (66% of invert ratios), 8 hours, 19 hours (93%), 28 hours, and 100 hours.

[0075] By the copolymerization system with which a multi-styrene macro monomer is concerned, the weight average molecular weight exceeds 10,000, and the result of drawing 1 shows that it is larger than weight average molecular weight (5000) in case the invert ratio of the styrene in a homopolymerization system is 93%, although a styrene invert ratio is 25% in reaction 2 hours. Furthermore, a GPC chart is shifted to a macromolecule side along with the increment in reaction time, and it turns out that molecular weight increases with time amount.

[0076] That is, as for a growth radical, the polymerization system with which a multi-styrene macro monomer is concerned also has living nature, and the place where the invert ratio of a styrene monomer is still low shows growing, while a multi-styrene macro monomer is concerned with copolymerization. Especially in the place where the reaction advanced for 19 hours, the maximum molecular weight which is the beginning of the curve by the giant-molecule side in GPC was set to 2613000, and amounted to 10104000 exceeding 10 million after 4443000 or 100 hours after 28 hours.

[0077] The result of drawing 1 of an example 6 showed that it increased in the same direction in the living radical polymerization of the

styrene with which a multi-styrene macro monomer is concerned to the invert ratio and molecular weight for every time amount of the olefin functional group, and increase of molecular weight showed further that it flew up greatly after fixed time amount. therefore, letter of branching - of the two-dimensional "island-suspension bridge" mold which is the homopolymerization system of an olefin monomer and is not obtained by the radical polymerization system using a multi-styrene macro monomer -- a line -- a hybrid polymer can be manufactured easily.

[0078] Furthermore, molecular weight which a GPC chart begins was made into the maximum molecular weight, and correlation with the invert ratio of it and styrene and polymerization reaction time was shown in drawing 2 . Although the invert ratio of styrene increased smoothly along with increase of reaction time, the maximum molecular weight increased by leaps and bounds in the place which it passes fixed time. That is, existence of a macro monomer shows jumping the molecular weight of a copolymer suddenly along with increase of time amount or an invert ratio. It is thought that this phenomenon suggests strongly the polymerization reaction process in which it joins with suspension bridge structure in macro monomers.

[0079] (Example 7) [-- letter of branching - of I2-MS and methyl methacrylate depended a radical copolymerization system -- a line -- the eggplant mold flask equipped with synthetic] MAG stirring child of a hybrid polymer (cable address--I2-MS-MMA -6) -- a nitrogen purge -- carrying out -- it -- I2-MS of the 1.3 weight section, the azobis isobutyl nitril of the 0.51 weight sections, and 50.8 weight sections methyl methacrylate The toluene of the 50.8 weight sections was added and the mixed solution was prepared. Stirring this mixed solution by the stirrer, it heated with the 100-degree C oil bath, and was made to react for 15 minutes. When polymerization reaction mixture was measured in 1H NMR, the invert ratio of a methyl methacrylate monomer was 78%.

[0080] This polymer was settled in a lot of hexanes, and suction filtration washed the polymer solid. After drying a polymer at a room temperature, under the vacuum, it was made to dry for 24 hours and 60 degree C of polymer P-I2-MS-MMA -6 were obtained with 73% of yield. The weight average molecular weight in GPC of a polymer (P-I2-MS-MMA -6) was 325000, and molecular weight distribution were 15.5.

[0081] (Example 5 of a comparison) The weight average molecular weight of the polymethylmethacrylate obtained without the macro monomer by homopolymerization of only methyl methacrylate was 15000 under the condition same as a control experiment as the same preparation as an example 6, and molecular weight distribution were 1.76.

[0082]

[Effect of the Invention] This invention can provide a solvent with a meltable new copolymer and its manufacturing method, having high molecular weight by carrying out copolymerization of the multi-branch-type multi-styrene macro monomer to an olefin system monomer.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing change of the GPC chart by the polymerization time amount of the copolymer of an example 6. As for the GPC chart of the styrene homopolymerization system (reaction 4 hours, 93% of invert ratios) of the example of a comparison, and the curve of the second henceforth, the top curve shows the GPC chart in each reaction time of a copolymerization system. The axis of abscissa of drawing shows the holding time (minute) of GPC.

[Drawing 2] It is drawing showing the invert ratio of a styrene monomer and the change of the maximum molecular weight by the polymerization time amount of the copolymer of an example 6. As for the axis of abscissa of drawing, (%) and the invert ratio of a styrene monomer, and a right longitudinal shaft show the maximum molecular weight ($\times 10^3$), as for polymerization time amount (h) and a left axis of ordinate.

[Translation done.]

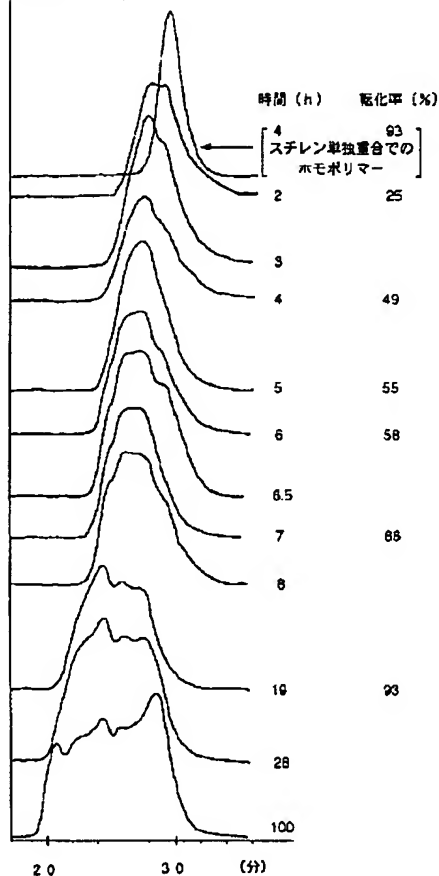
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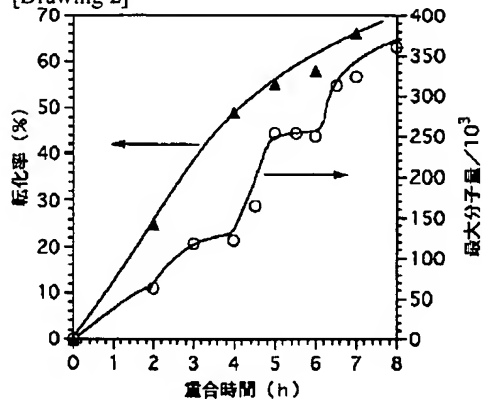
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DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]